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Can coupled cluster singles and doubles be approximated by a valence active space model?

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A new, efficient approximation for coupled cluster singles and doubles (CCSD) is proposed in which a CCSD calculation is performed in a valence active space followed by a second-order perturbative correction to account for the inactive singles and doubles cluster amplitudes. This method, denoted VCCSD(SD), satisfactorily reproduces CCSD results in a variety of test cases, including spectroscopic constants of diatomic molecules, reaction energies, the Cope rearrangement, and other relative energies. Use of VCCSD alone is significantly less satisfactory. Formally, the O^2V^4 scaling of CCSD is reduced to $o^2v^2V^2$, where o is the number of active occupied orbitals, v is the number of active virtual orbitals, and V is the total number of virtual orbitals. We also investigate the role of orbital optimizations and the appropriate choice of an active space in such methods. © *2002 American Institute of Physics.* [DOI: 10.1063/1.1493181]

I. INTRODUCTION

Despite recent advances in computer hardware, accurate *ab initio* electronic structure calculations on large molecules remain difficult due to the high formal scaling of the computational cost of standard wave function-based correlation methods. The widely used second-order Møller–Plesset perturbation theory (MP2) scales formally as N^5, and the generally more accurate coupled cluster singles doubles (CCSD) method scales as N^6, where N is the number of basis functions. However, these formal scalings are unphysical,[1] and one would like to reduce this formal scaling using appropriate physical and numerical approximations.

One such approach to reducing this high cost has been through the so-called local correlation methods pioneered by Saebø and Pulay.[2,3] In methods of this type, molecular orbitals are localized in some fashion and excitation amplitudes (whether in the context of MP2 or coupled cluster theories) are explicitly treated only between orbitals within some predefined spatial distance. Though highly efficient and often quite accurate,[4] these methods contain a degree of arbitrariness in how these cutoffs are defined and also can produce discontinuous potential energy surfaces as molecular geometry changes.[3] These problems can be avoided at additional computational cost by utilizing different criteria for selecting significant excitation amplitudes. One such model implemented for MP2 is the TRIM model,[5] in which only double excitations with one occupied and one virtual orbital on a common atom are retained. Another alternative is to use atomic orbital basis cutoffs directly.[6,7]

The purpose of this paper is to explore whether efficient approximations to CCSD can be formulated in a two-stage approach, similar to that employed in methods which first treat static correlation in an active space, followed by dynamical correlations associated with orbitals outside the active space. This is the strategy used in the CASSCF/CASPT2 pair of methods, for example.[8] However, instead of the factorially expensive CASSCF treatment of the active electrons,[9] we will use CCSD itself in the space of all valence orbitals. A subsequent second-order correction outside the valence space will be performed using our recently developed similarity-transformed perturbation theory.[10–13]

The motivation for doing this is both physical and algorithmic. We expect that beyond-valence correlations are weaker and will thus be more satisfactorily treated by perturbation theory than valence correlations. Furthermore, within the valence space, approximations to CCSD can be stronger than in the full space—for example the perfect pairing generalized valence bond (PP-GVB) approximation[14–17] retains only a linear number of pair excitations. Generalizations to restricted pairing[18–20] retain only a small quadratic number of amplitudes. Thus, one can potentially combine the ability of these methods to treat very large active spaces with local MP2-type models for the beyond-valence correlation.

This paper takes the first step towards this general objective by addressing the extent to which an approximation of this type can be faithful to full CCSD. We do this by first obtaining an appropriate set of valence orbitals (in the 1:1 active space, where each valence occupied orbital is associated with a correlating antibonding orbital, as in perfect pairing). The reference CCSD calculation is performed in this limited valence space, with no local approximations. Subsequently, the second-order perturbative correction is performed with only single and doubles terms as needed to mimic full CCSD. This hybrid theory is defined in the following section, and its computational cost in the absence of local approximations is discussed. It is then tested against full CCSD for a range of structural and energetic properties.

II. THEORY

Our target level of theory is the standard CCSD method, which involves a wave function of the following form:

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$$|\Psi_{\mathrm{CC}}\rangle = e^{\hat{T}}|\Phi_0\rangle, \tag{1}$$

$$\hat{T} \equiv \hat{T}_1 + \hat{T}_2 = \sum_{i,a} t_i^a \{\hat{a}_a^\dagger \hat{a}_i\} + \frac{1}{4}\sum_{i,j,a,b} t_{ij}^{ab}\{\hat{a}_a^\dagger \hat{a}_i \hat{a}_b^\dagger \hat{a}_j\}, \tag{2}$$

Here $i,j,k,\ldots,$ refer to occupied orbitals, and $a,b,c,\ldots,$ refer to virtual orbitals. The energy and unknown cluster amplitudes are obtained by minimizing the functional

$$F_{\mathrm{CCSD}} = \langle \Phi_0|(1+\hat{\Lambda})e^{-\hat{T}}\hat{H}e^{\hat{T}}|\Phi_0\rangle, \tag{3}$$

where

$$\hat{\Lambda} \equiv \hat{\Lambda}_1 + \hat{\Lambda}_2 = \sum_{i,a} \lambda_a^i \{\hat{a}_i^\dagger \hat{a}_a\} + \frac{1}{4}\sum_{i,j,a,b} \lambda_{ab}^{ij}\{\hat{a}_i^\dagger \hat{a}_a \hat{a}_j^\dagger \hat{a}_b\}, \tag{4}$$

by forcing the derivatives of the functional with respect to the λ and t amplitudes to be stationary. Symbolically, this may be written as

$$\frac{\partial F_{\mathrm{CCSD}}}{\partial \hat{\Lambda}} = 0, \quad \frac{\partial F_{\mathrm{CCSD}}}{\partial \hat{T}} = 0. \tag{5}$$

In CCSD, the occupied orbitals may be restricted to only valence orbitals (e.g., a frozen core approximation), but no restrictions are usually imposed on the virtual orbitals.

We approximate the full solution of the CCSD equations in two stages. The first step is to solve the CCSD problem in just a valence space. In other words, we restrict the t and λ amplitudes such that excitations occur only within an active space of valence orbitals. The second step is the addition of a perturbative second-order correction for beyond-valence correlation.

We consider that active spaces appropriate for general chemical applicability are ones which correlate all valence electrons. Two principal alternatives are the full valence (V) active space and the perfect-pairing or (1:1) active space (PP). Disregarding spatial symmetry, the full valence space defines the active orbitals to be equal to the number of valence atomic orbitals. The PP space (for closed-shell molecules) defines the number of active orbitals to be twice the number of occupied valence orbitals, where there is (at least in principle) one correlating orbital for each occupied orbital.

To apply CCSD within a valence active space means that the active orbitals must have been optimized by another method. After all, one should not simply choose the lowest virtual orbitals from a Hartree–Fock calculation to be the active orbitals. As the basis set size grows, these lowest-lying virtual orbitals become low-energy, diffuse Rydberg orbitals which cannot properly correlate occupied valence bonding orbitals. Correspondingly, the magnitude of the correlation energy from such a calculation limits toward zero as the basis set approaches completeness—clearly an unphysical result!

Several reasonable choices for valence optimized orbitals are possible. First, one could choose orbitals from a valence optimized orbital CCD (VOD)[21] or QCCD[22] calculation. However, these calculations are still relatively expensive. In particular, they are far more expensive than performing CCSD in the valence space, presuming the orbitals are available. It is therefore expedient to use a strong local correlation approximation, which will permit (relatively) inexpensive optimization of the valence active space. The local correlation approximation need not be quantitatively accurate; it must simply yield a reasonably faithful set of valence orbitals.

One such possibility is perfect-pairing CCD, which yields approximate PP orbitals, based on retaining only a linear number of amplitudes.[18,23,24] A related possibility is to use imperfect-pairing (IP) CCD, which also determines approximate PP orbitals, but based on retaining a quadratic number of double excitations.[18] Because of the increased flexibility in the IP functional, the orbitals obtained have been found to be closer to the VOD-optimized orbitals, and we therefore adopt it as our source of valence optimized orbitals. We therefore also adopt the PP active space. In summary, VCCSD calculations involve optimization of the PP active space within the IP ansatz followed by CCSD with no local correlation approximations in this valence space.

As the VCCSD calculation is performed only within the PP valence space, it recovers only a modest fraction of the total correlation energy, perhaps in the vicinity of 20% to 40% and diminishing with larger basis sets. Valence correlation can be viewed as a definition of static or nondynamical correlation energy. To approach quantitatively accurate results, it is likely that a correction must be applied subsequent to VCCSD to account for the beyond-valence or dynamical correlations. We apply a perturbative, second-order correction based on our recently introduced similarity transformed perturbation theory.[11,12]

The resulting equations have the following general form:

$$E^{[0]} = E_{\mathrm{VCCSD}}, \tag{6}$$

$$E^{[1]} = 0, \tag{7}$$

$$E^{[2]} = \langle 0|(1+\Lambda)\overline{H}^{[1]}(E^{[0]} - \overline{H}^{[0]})^{-1}\overline{H}^{[1]}|0\rangle. \tag{8}$$

This correction contains terms involving single, double, triple, and quadruple excitations, as discussed in detail elsewhere.[11]

Since our goal is to approximate CCSD efficiently, we truncate this correction after the doubles terms, ignoring the computationally demanding triples and quadruples terms which are not present in CCSD. We term this procedure VCCSD(SD). Evaluation of the (SD) correction dominates the computational time. Overall, the method scales as $o^2v^2V^2$, where o is the number of active occupied orbitals, v is the number of active virtual orbitals, and V is the total number of virtual orbitals. In separate future work we will include the triples and quadruples terms to assess their ability to directly approximate CCSD(2) (Ref. 12) [which is equivalent or superior to CCSD(T) (Ref. 25)] from a VCCSD starting point.

III. RESULTS AND DISCUSSION

The VCCSD(SD) method has been implemented in a developmental version of Q-CHEM.[26] A variety of tests has been performed in order to determine the accuracy with which VCCSD(SD) approximates standard CCSD results.

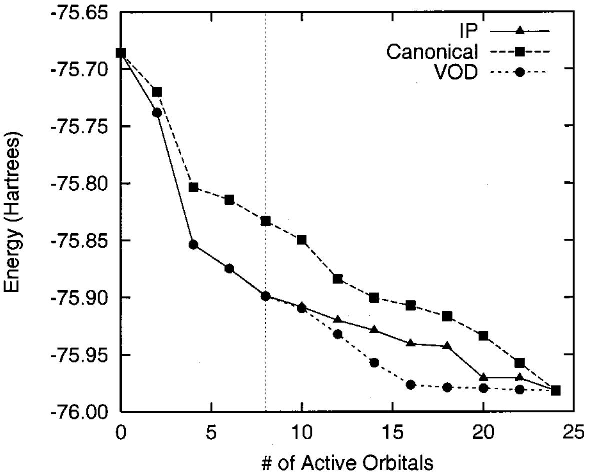

FIG. 1. Energies as a function of active space size for H_2O, symmetrically stretched to $1.75R_e$, in a cc-pVDZ basis as calculated with VCCSD using IP orbitals, VCCSD using canonical orbitals, and VOD. The active space contains equal numbers of occupied and virtual orbitals until all five occupied orbitals are active, after which only virtual orbitals are added to the space. The vertical dashed line marks the PP active space used in a standard VCCSD calculation.

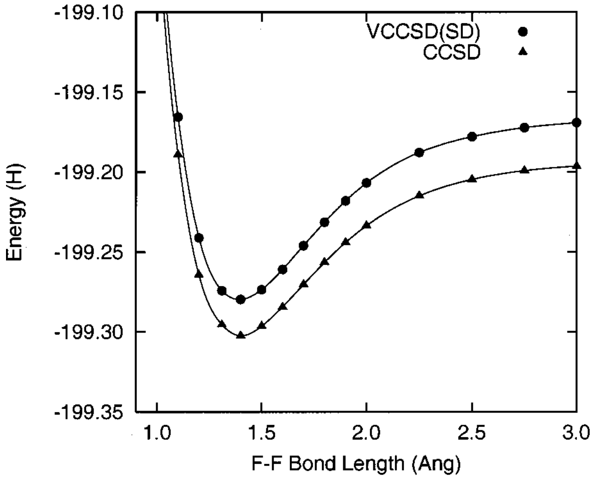

FIG. 2. The F_2 potential produced by stretching the F–F bond in a cc-pVTZ basis.

We also make some very preliminary tests of computational efficiency. Each of these is described below. In some cases, it is desirable to compare the results obtained with VCCSD(SD) againsst those obtained from a method where the active orbitals are fully optimized (and therefore represent the best choice of orbitals for such a method). For this reason, we also introduce VOD(SD), which is equivalent to VOD(2) (Ref. 11) except that the perturbation correction is truncated as described above for VCCSD(SD).

A. The VCCSD energy and the choice of active space

The performance of any active space method depends critically upon the choice of the orbitals within that space. Here, we address this issue in the context of VCCSD. Figure 1 plots the VCCSD and VOD energy (without the perturbative correction) versus the active space size for water in a cc-pVDZ basis.[27,28] In this example, the water molecule has been symmetrically stretched to $1.75R_e$, thereby increasing the significance of the static correlation. The active space used is of the perfect-pairing (1:1) type until ten orbitals are active. Beyond this point, all occupied orbitals are active, so only the active virtual space grows. With no active orbitals we obtain the Hartree–Fock result, and with all 24 orbitals active we have the CCSD result.

Focusing first on the VOD curve in Fig. 1, we see a dramatic gain in correlation energy at four active orbitals, corresponding to the inclusion of a correlating virtual for each pair of bonding electrons. Doubling the active space size to eight orbitals (the PP active space) adds in correlating orbitals for the lone pairs and obtains significantly more correlation energy. Although no rigorous partitioning of the static and dynamical correlation exists, this chemically motivated active space translates into a suitable choice for obtaining a sizable fraction of the correlation energy roughly corresponding to the static correlation at minimal cost. Alternatively, once might consider something like a "double-PP" active space with 16 active orbitals instead of eight, thereby providing three correlating orbitals to each occupied. In this case, a double-PP active space would recover almost all of the CCSD correlation energy. However, exploration of such extended active spaces will be the subject of future studies. For now, the remaining (dynamical) correlation will be obtained with perturbation theory.

VCCSD with the IP-optimized orbitals behaves qualitatively the same as VOD up through ten active orbitals (i.e., in the regime in which IP is well defined). Beyond ten active orbitals, no more occupied orbitals remain to pair with additional virtual orbitals, so subsequent active virtuals have little chemical significance in the IP model. Correspondingly, the rate of correlation energy recovery drops dramatically. Thus, the approximately optimized orbitals (from an IP calculation) behave similarly to the fully optimized orbitals within the PP active space. As for VOD, this choice of active space balances efficiency and recovery of the correlation energy. In contrast, if we use the canonical orbitals instead, the active space must be roughly twice as large to recover the same portion of the correlation obtained with IP orbitals in the PP space, underscoring the importance of an optimized active space.

B. Potential energy surfaces and spectroscopic constants of diatomic molecules

Next, we focus on the ability of VCCSD and VCCSD(SD) to reproduce CCSD potential energy surfaces and properties. Consider, for example, the surface produced by stretching the F_2 bond, as shown in Fig. 2. Qualitatively, VCCSD(SD) reproduces the shape of the CCSD potential, though the absolute energy is somewhat in error. However, this absolute error in energy is, for the most part, unimportant in observable relative energies, as demonstrated below. First, we focus on the ability of VCCSD and VCCSD(SD) to correctly mimic the CCSD potentials in calculating the spec-

TABLE I. Root-mean-square errors with respect to CCSD for VCCSD(SD) and MP2 for first- and second-row diatomic spectroscopic constants. R_e is in Å, while the other properties are in cm^{-1}.

	R_e	ω_e	B_e	D_e	α_e	$\omega_e x_e$
MP2[a]	0.0083	89.2	0.077	13.2×10^{-6}	0.0139	2.55
VCCSD[a]	0.0086	43.1	0.143	10.4×10^{-6}	0.0067	2.83
VCCSD(SD)[a]	0.0040	21.8	0.020	2.89×10^{-6}	0.0032	0.72
MP2[b]	0.0145	71.1	0.019	2.59×10^{-6}	0.0034	1.02
VCCSD[b]	0.0193	37.2	0.0830	4.53×10^{-6}	0.0076	2.81
VCCSD(SD)[b]	0.0085	13.7	0.005	1.49×10^{-6}	0.0032	1.17
MP2[c]	0.0242	107.9	0.0321	6.64×10^{-6}	0.0059	2.38
VCCSD[c]	0.0425	51.9	0.1379	6.67×10^{-6}	0.0032	9.61
VCCSD(SD)[c]	0.0175	22.9	0.0190	2.12×10^{-6}	0.0022	2.62

[a] Includes: BF, BH, C_2, CO, F_2, HF, N_2, NF, and NH, in the cc-pCVTZ basis.

[b] Includes: AlCl, AlF, AlH, Cl_2, CS, FCl, HCl, NP, P_2, SiO, and SiS, in the cc-pV(T+d)Z basis (Al–Cl) and the cc-pCVTZ basis (H–F).

[c] Includes: BeO, BeS, Li_2, LiH, MgO, MgS, Na_2, NaF, NaH in the 6-311G($2df$,$2pd$) basis.

troscopic constants R_e, ω_e, B_e, D_e, α_e, and $\omega_e x_e$ for the singlet ground-state first- and second-row diatomic molecules.

Five single-point calculations about the experimental R_e values[29] spaced 10 picometers apart were used for the fit, which was performed with PSI.[30] In cases where the points were not well centered about the experimental minimum, a shifted set of points was used to obtain better results. Unfortunately, the target cc-pCVTZ basis[27,31] is unavailable for many of the elements in this study. Therefore, the cc-pV($T+d$)Z basis[32] and the 6-311G($2df$,$2pd$) basis[33,34] were used as well. For the purpose of calculating statistics, the diatomics are divided into three groups based on the basis sets used, as explained in Table I. The first group of diatomics contains BF, BH, C_2, CO, F_2, HF, N_2, NF, and NH, the second group contains AlCl, AlF, AlH, Cl_2, CS, FCl, HCl, NP, P_2, SiO, and SiS, and the third group contains BeO, BeS, Li_2, LiH, MgO, MgS, Na_2, NaF, and NaH. We compare VCCSD, VCCSD(SD), and MP2 results against CCSD results, since our aim is to test the faithfulness of VCCSD(SD) to CCSD rather than to concern ourselves with choosing appropriate basis sets for predicting experimental results. Mg_2 is excluded from the study because it was found that each theory predicted widely different bond lengths ranging from 4.5 to 7.5 Å, none of which was near the experimental value of 3.89 Å. Further study of this molecule is beyond the scope of this paper.

Table I contains the root-mean-square (rms) errors for MP2, VCCSD, and VCCSD(SD) as compared to the CCSD results for each group of diatomic molecules and each spectroscopic constant. For almost every constant, VCCSD(SD) results are a factor of 2 to 4 better overall than their corresponding MP2 results. Note particularly the success of VCCSD(SD) in predicting harmonic frequencies, rotational constants, and centrifugal distortion constants as compared to MP2. The anharmonic and coupling constants prove slightly more difficult for VCCSD(SD). The second and third groups of anharmonic constants are the only categories in which MP2 has a lower rms error than VCCSD(SD), primarily due to AlH, for which VCCSD(SD) is 3.4 cm^{-1} (15.5%) off and Li_2, for which it is 6.1 cm^{-1} in error. However, the other VCCSD(SD)-calculated properties of AlH are in fairly good agreement with CCSD, so this case is not too significant. Moreover, the error in Li_2 is large but qualitatively correct. In contrast, MP2 predicts the wrong sign for this constant. The largest errors for VCCSD(SD) occur in the third group, which contains molecules with alkali and alkaline earth metals. This is not surprising, since the PP active spaces for these elements are quite small. Nevertheless, VCCSD(SD) generally outperforms MP2 even in these cases.

One molecule, AlCl, deserves closer examination. VCCSD(SD) has particular difficulty with AlCl, as shown by the results in Table II. The fit for AlCl was performed on points every 10 picometers from 2.100 113 to 2.140 113 Å, rather than the standard five single points centered about the experimental equilibrium bond length (2.130 113 Å). In any case, VCCSD(SD) does not correctly reproduce the potential

TABLE II. Predicted spectroscopic constants for AlCl in the cc-pV($T+d$)Z basis. R_e is in Å, while the other properties are in cm^{-1}.

	R_e	ω_e	B_e	D_e	α_e	$\omega_e x_e$
MP2	2.136 411	489.9	0.242 51	0.238×10^{-6}	0.001 50	1.87
VCCSD(SD)	2.113 053	517.5	0.247 90	0.228×10^{-6}	0.001 93	0.78
VOD(SD)	2.115 792	492.7	0.247 26	0.249×10^{-6}	0.001 54	1.86
CCSD	2.137 953	490.1	0.242 16	0.236×10^{-6}	0.001 49	1.99
Experiment[a]	2.130 113	481.3	0.243 93	0.250×10^{-6}	0.001 611	1.95

[a] Values taken from Ref. 29.

TABLE III. Calculated harmonic frequencies ω_e using MP2, VCCSD, VCCSD(SD), and CCSD. CCSD value is the calculated one, while other columns are errors relative to CCSD. All values are in cm^{-1}. The molecules are grouped by basis set as described in Table I and in the text.

	MP2	VCCSD	VCCSD(SD)	CCSD
BF	−3.47	−25.91	15.00	1427.36
BH	67.46	−90.10	−6.56	2367.86
C_2	−2.83	−9.62	46.54	1891.93
CO	−101.77	−6.38	16.79	2233.30
F_2	0.51	−57.95	13.10	1020.64
HF	−34.26	−14.04	6.12	4214.75
N_2	−226.73	−37.73	6.62	2434.33
NF	22.01	20.26	34.50	1243.21
NH	60.36	−49.40	−11.30	3357.84
AlCl	−0.22	−8.38	27.37	490.10
AlF	−13.61	−9.73	0.56	801.94
AlH	28.61	−69.63	−15.67	1672.66
Cl_2	13.88	−63.20	18.13	572.21
CS	−27.71	−8.14	4.42	1359.65
FCl	−3.25	−1.54	−24.43	813.55
HCl	32.39	−41.28	−6.48	3027.38
NP	−196.82	−35.27	3.86	1400.05
P_2	−78.26	−53.37	6.68	821.09
SiO	−86.14	−5.37	5.82	1290.01
SiS	−19.18	−18.74	−0.94	778.90
BeO	−146.68	−20.05	9.70	1583.17
BeS	−18.01	−23.44	7.64	1020.36
Li_2	−12.13	0.67	−3.81	353.09
LiH	30.07	−112.09	−17.38	1416.22
MgO	282.72	8.77	55.46	746.49
MgS	30.78	−47.99	29.37	527.46
Na_2	−2.23	−1.20	8.55	159.28
NaF	−3.02	−9.95	−2.74	578.41
NaH	30.37	−90.84	−15.05	1158.69

TABLE IV. Calculated anharmonic constants $\omega_e x_e$ using MP2, VCCSD, VCCSD(SD), and CCSD. CCSD value is the calculated one, while other columns are errors relative to CCSD. All values are in cm^{-1}. The molecules are grouped by basis set as described in Table I and in the text.

	MP2	VCCSD	VCCSD(SD)	CCSD
BF	0.14	−0.88	0.30	11.12
BH	−2.17	−6.67	0.66	48.30
C_2	−1.14	−0.97	−0.27	12.42
CO	0.45	−0.96	0.81	12.11
F_2	−0.58	2.35	−0.91	9.81
HF	−3.80	−3.74	1.23	89.85
N_2	4.45	−0.38	−0.09	13.27
NF	−0.13	−0.20	0.75	9.30
NH	−4.19	−2.31	0.67	75.54
AlCl	−0.12	−3.11	−1.21	1.99
AlF	−0.44	−0.27	0.16	4.06
AlH	0.25	8.57	3.37	21.64
Cl_2	0.05	0.14	−0.14	2.33
CS	−0.20	0.20	0.13	6.02
FCl	−0.25	0.73	−0.51	4.56
HCl	−1.45	−0.03	−0.20	52.23
NP	2.85	1.68	1.24	6.20
P_2	0.86	−0.25	−0.19	2.54
SiO	0.06	−0.32	0.08	5.35
SiS	0.02	0.24	0.51	2.28
BeO	1.69	−0.89	0.26	11.07
BeS	−1.98	−0.96	−0.53	6.44
Li_2	−3.21	0.91	6.10	1.79
LiH	−2.37	−3.62	−2.03	25.14
MgO	4.05	3.35	1.36	0.66
MgS	−1.49	−26.49	1.48	2.76
Na_2	−0.52	−1.61	2.55	−0.69
NaF	−0.14	−0.44	0.06	3.36
NaH	−3.06	−10.00	3.10	14.66

surface. For comparison, VOD(SD) was run to determine whether the problem stems from the partitioning of the correlation energy or whether it is due to the difference between IP orbitals and fully optimized orbitals (as in VOD). We see that while VOD(SD) does fix the problem somewhat, especially in ω_e and $\omega_e x_e$, the other properties still differ substantially from CCSD. Apparently, AlCl does not lend itself well to a partitioned description of its correlation energy, at least in the perfect-pairing active space.

In contrast to the fairly systematic improvement of the results going from MP2 to VCCSD(SD), the uncorrected VCCSD behaves quite inconsistently. Although in a few cases it performs reasonably well, it generally fluctuates significantly, leading to rather large rms errors as shown in Table I. For example, VCCSD improves upon the MP2 description of harmonic frequencies, but it errs grossly in the rotational constants. The anharmonic constants are also poor in most cases. The valence correlation alone is insufficient to quantitatively describe potential energy surfaces and their associated spectroscopic constants (although it is of course better than no correlation at all).

We also present Tables III and IV containing the actual computed values of ω_e and $\omega_e x_e$, which are representative of the best and worst cases for VCCSD(SD). For harmonic frequencies, the largest VCCSD(SD) errors are roughly 50 cm^{-1} for C_2 and MgO. In contrast, MP2 has errors of over 100 cm^{-1} or more for several molecules, including CO, N_2, NP, and MgO. In the last case, the VCCSD(SD) error is one-fifth the size of the MP2 one. For uncorrected VCCSD, the errors are smaller than those for MP2, but larger errors on the order of 50 cm^{-1} or more are quite common, including most of the hydrides, N_2, P_2, and MgS. While MP2 and VCCSD(SD) tend to give fairly good results for a range of molecules with intermittent exceptions, VCCSD gives mediocre or poor results for a large number of cases. Looking at the harmonic constants in Table IV, we again see that for most molecules the methods are fairly good, though each, has its exceptions. Notably, VCCSD predicts the wrong sign of $\omega_e x_e$ for AlCl, MgS, and Na_2. Actually, in the case of Na_2, CCSD, MP2, and VCCSD all predict a negative $\omega_e x_e$. The experimental value, however, is 0.725 cm^{-1}. Only VCCSD(SD) gets the appropriate sign even if it is about twice as large as the experimental value. The largest MP2 error is MgO, at 4.0 cm^{-1}, while the largest VCCSD error is 26.5 cm^{-1} for MgS, and the largest VCCSD(SD) error is 6.1 cm^{-1} for Li_2. Overall, while the difference between VCCSD(SD) and MP2 is less clear here, VCCSD(SD) performs as well as or slightly better than MP2 on the whole.

In summary, VCCSD(SD) successfully reproduces the full CCSD spectroscopic properties of first- and second-row

TABLE V. Reaction energies for isogyric reactions in the aug-cc-pVDZ basis. Errors are relative to CCSD results. Energies are in kcal/mol. Reactions taken from Ref. 35 and the geometries from Ref. 36.

Reaction	MP2	VCCSD	VCCSD(SD)	VOD(S)	CCSD
$CO+H_2\rightarrow CH_2O$	−3.085	1.589	−3.773	−3.289	−2.432
$N_2+3H_2\rightarrow 2NH_3$	−39.192	−26.329	−40.436	−40.827	−40.325
$C_2H_2+H_2\rightarrow C_2H_4$	−50.923	−40.190	−51.000	−51.389	−53.750
$CO_2+4H_2\rightarrow CH_4+2H_2O$	−60.706	−51.571	−65.353	−64.137	−66.246
$CH_2O+2H_2\rightarrow CH_4+H_2O$	−63.954	−56.129	−63.901	−63.734	−63.659
$CO+3H_2\rightarrow CH_4+H_2O$	−67.039	−54.541	−67.674	−67.023	−66.092
$HCN+3H_2\rightarrow CH_4+NH_3$	−76.505	−60.811	−77.205	−77.233	−79.291
$H_2O_2+H_2\rightarrow 2H_2O$	−137.678	−142.786	−139.381	−139.191	−136.010
$HNO+2H_2\rightarrow H_2O+NH_3$	−181.830	−178.817	−180.785	−180.347	−178.307
$C_2H_2+3H_2\rightarrow 2CH_4$	−110.558	−91.631	−109.311	−109.339	−113.645
$CH_2(^1A_1)+H_2\rightarrow CH_4$	−133.405	−118.912	−126.818	−126.544	−125.228
$F_2+H_2\rightarrow 2HF$	−143.647	−148.854	−141.691	−141.502	−138.327
$2CH_2(^1A_1)\rightarrow C_2H_4$	−207.175	−186.397	−195.326	−195.138	−190.562
Mean absolute error	4.044	10.316	2.224	2.114	
rms error	5.851	11.902	2.630	2.507	

diatomic molecules. VCCSD(SD) is clearly superior to MP2 bond lengths, harmonic frequencies, rotational constants, and centrifugal distortion constants, and as good or better for the anharmonic and vibration–rotation coupling constants.

C. Relative energies

To further test the faithfulness of VCCSD(SD) to standard CCSD, reaction energies for a series of 13 isogyric reactions[35] were calculated with MP2, VCCSD, VCCSD(SD), VOD(SD), and CCSD using accurate equilibrium geometries,[36] the results of which are shown in Table V. Once again, we see a substantial improvement in accuracy relative to CCSD in going from MP2 to VCCSD(SD) and VOD(SD) in terms of the mean absolute error and the root-mean-square deviations. In fact, VOD(SD) and VCCSD(SD) behave rather similarly, though VOD(SD) does slightly better on the whole, as would be expected. More importantly, VCCSD without the perturbative correction is clearly unable to accurately reproduce the relative energies of these reactions. The first reaction energy even has the wrong sign. By itself, the valence space calculation is an insufficient model for the correlation energy. For four of the 13 reactions, MP2 actually gets closer to the CCSD results than VCCSD(SD), but in most cases the difference between the two methods is rather small. Overall, VCCSD(SD) seems to satisfactorily reproduce CCSD reaction energies.

A more sensitive test of the accuracy of any method is its ability to accurately predict small relative energies such as torsional barrier. As an example, we focus on the torsional barrier of ethane rotating from the *anti* to *gauche* configurations. Table VI compares the results for the torsional barrier of ethane for MP2, VCCSD(SD), VOD(SD), and CCSD with multiple basis sets. Once again, VCCSD(SD) [and VOD(SD)] performs much better than MP2 relative to the CCSD results, with errors of roughly half a percent versus 2%–3% for MP2. Although in this case the absolute errors are rather small, the faithfulness of VCCSD(SD) to CCSD is encouraging. In contrast, VCCSD seems to perform rather erratically, sometimes doing very well and sometimes behaving more like MP2, demonstrating once again the importance of the perturbative correction.

D. Benzene and symmetry

Using a strong local correlation approximation for the valence correlation energy is known to sometimes introduce artifacts in computed potential energy surfaces. One classic example is that both IP and PP-GVB predict broken symmetry in benzene—that is, they predict alternating longer and shorter bonds as a stable structure as a result of the localization procedure and the restrictions placed on the cluster amplitudes.[18] This deformation can be represented as a deviation of the bond angles from 60 deg to alternating angles of $60+\phi$ and $60-\phi$. What impact, if any, does the use of these IP orbitals have on VCCSD(SD)?

The results of such calculations are shown in Fig. 3, where the energy of benzene is calculated versus the defor-

TABLE VI. Torsional barrier of ethane under *anti* to *gauche* rotation with increasing basis set size. Energies are in kcal/mol. Percent errors relative to CCSD are in parentheses.

	cc-pVDZ[a]		aug-cc-pVDZ[a]		cc-pVTZ[a]	
MP2	3.744	(3.13)	3.570	(2.21)	3.447	(2.01)
VCCSD	3.603	(−0.74)	3.586	(1.03)	3.371	(−0.24)
VCCSD(SD)	3.610	(−0.55)	3.485	(−0.20)	3.364	(−0.45)
VOD(SD)	3.597	(−0.92)	3.473	(−0.54)	3.349	(−0.89)
CCSD	3.630		3.492		3.379	

[a] Reference 27.

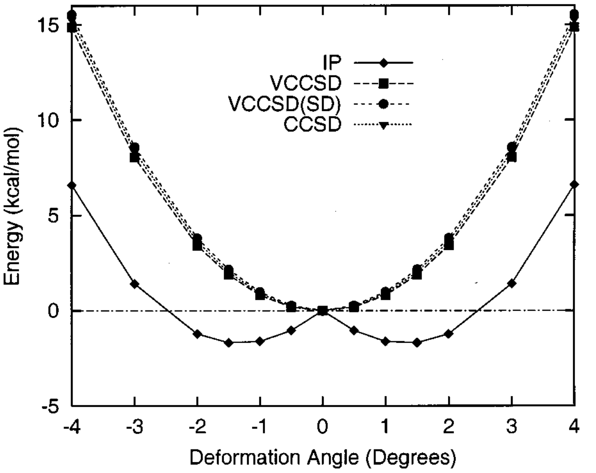

FIG. 3. Deformation of benzene and symmetry breaking. Calculations performed in a 6-31G* basis (Refs. 44, 45) and with radial distances fixed at the MP2/6-31G* level. The symmetry-breaking angle is described in the text.

mation angle ϕ. The VCCSD(SD) results for the deformation of benzene correctly restore symmetry to benzene. This is because excitations from one localized bonding orbital are allowed to occur to localized antibonding orbitals on other sites in the VCCSD calculation, thereby returning to the picture of delocalized bonding. Thus, we see no serious consequences from using the IP orbitals for VCCSD(SD) in this case where the IP potential surface itself is incorrect.

E. The Cope rearrangement

Having demonstrated the performance of VCCSD(SD) on simple systems, we shift our attention to a more difficult example: the Cope rearrangement. This reaction has been the focus of many studies at different theoretical levels including semiempirical, DFT, and multireference methods.[37–41] Unfortunately, the results of many of these studies contradicted one another both qualitatively and quantitatively, and only recently has the controversy been mostly resolved.[42] The difficulty arises because of the very flat energy landscape along a C_{2h} cut in the potential energy surface that connects a diyl intermediate at $R=1.64$ Å and an aromatic transition state at $R=2.19$ Å.[38,40] One way of exploring the success of various levels of theory in this reaction is to follow the C_{2h} cut of the surface between these two structures. Both RHF and UHF are inadequate since RHF cannot properly describe the diradicaloid species involved, and UHF overestimates the stability of such species.[42] Studies also suggest that correlated methods based on HF such as CCSD converge slowly with classes of excitation included.[43] Therefore, multireference methods have become standard in most of the accepted studies. As shown in the works cited above, a six-electron, six-orbital CASSCF calculation incorrectly places a small barrier between these two structures along the C_{2h} cut. The active space used includes the two π bonds and one σ bond explicitly involved in the rearrangement. However, they have shown that the addition of dynamical correlation through multireference perturbation theory eliminates this barrier, and predicts the true transition state for the Cope rearrangement (the minimum on this C_{2h} cut of the surface) to occur near 1.85 Å with a transition state barrier height of roughly 31 kcal/mol above hexadiene (the diyl and aromatic species lie at 33 and 35 kcal/mol, respectively).[40] This drastic change in behavior has been attributed to the dynamical correction allowing the sigma-bonding framework to relax during the reaction.[43] In a sense, this can be thought of as a triple excitation involving two active π electrons and an inactive σ one.

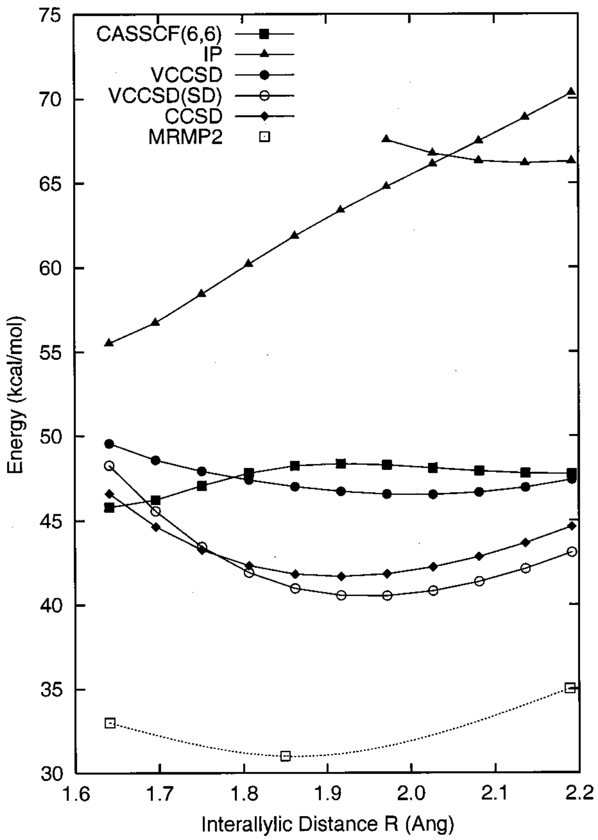

FIG. 4. C_{2h} cut along the Cope rearrangement potential energy surface. The CASSCF(6,6) and MRMP2 results are compared to IP, VCCSD, VCCSD(SD), and CCSD in the 6-31G* basis using the CCSD optimized geometries. Except for CASSCF, all the active space methods use the PP active space. The bond length R is the distance (in Å) between the two allyl groups in the chair structure, and energies are relative to hexadiene in kcal/mol. At short R is the diyl intermediate, and at long R is the aromatic species. The MRMP2 data were estimated from Ref. 40.

In this paper, we apply VCCSD and VCCSD(SD) to this reaction and compare against CCSD and the multireference methods. All calculations are performed at CASSCF(6,6)-optimized geometries using the 6-31G* basis at 11 geometries, with the interallylic distance ranging from 1.64 to 2.19 Å along the C_{2h} potential energy surface. In each case, restricted orbitals are used. VCCSD(SD) and related methods all use the PP active space, which contains 34 electrons in 34 orbitals for this system.

Figure 4 plots the C_{2h} potential energy surface as generated using CASSCF(6,6) and MRMP2, IP, VCCSD, and VCCSD(SD). In the figure, the MRMP2 minimum and end points were estimated from Ref. 40 and a smooth function interpolated between. The energies given are relative to the energy of hexadiene for each method. As discussed previously, CASSCF(6,6) places an unphysical barrier between the two intermediates. Not too surprisingly, IP performs poorly on this surface. We see two distinct states in this region: one roughly corresponding to the diyl and the other to the aromatic intermediate. Presumably, the occurrence of the second, lower-energy state in the aromatic region is a problem due to broken symmetry in the orbitals for the aromatic species, just as in benzene. The interesting question becomes, can VCCSD overcome this broken symmetry as in the benzene example? If we simply follow the lowest state at all times, the answer is no. VCCSD as calculated from these orbitals, though smoother than the IP surface, still demonstrates a kink where the orbitals break symmetry. In contrast, if we follow the symmetric (diyl) solution, VCCSD produces the smooth curve shown in Fig. 4. This curve is qualitatively similar to the MRMP2 surface,[40] except that the minimum on these two curves is rather long (occurring at just over 2 Å instead of 1.85 Å), and the relative energies of the end point intermediates are flipped (though the actual differences are only a few kcal/mol—well within the model errors). Despite the failure of the IP model, the orbitals so obtained are sufficient for VCCSD to obtain approximately the correct shape and relative energies of the intermediates as compared to the minimum, as long as one remains on the symmetry-preserving IP surface. Unfortunately, the energy of these states relative to hexadiene is much too high; VCCSD places the reaction transition state at roughly 46 kcal/mol (the minimum of the C_{2h} surface), in sharp disagreement with the approximately 31 kcal/mol reported by Kozlowski *et al.*[40]

Presumably, a better description could be obtained by including dynamical correlation. In the present context, we examine the effects of a partial treatment of dynamical correlation in the form of VCCSD(SD), the results of which are plotted in Fig. 4. Indeed, we see that the transition state barrier is lowered to about 41 kcal/mol (still high), but the aromatic species is much lower than the diyl one. Moreover, although the minimum moves to shorter interallylic distances, it is still longer than MRMP2. Although the perturbative singles and doubles terms are largely sufficient to describe the aromatic species, the more difficult diyl species presumably requires higher-order excitations in order to be described accurately. These results agree fairly well with those from CCSD, though CCSD shows a smaller difference between the two end points and a slightly shorter transition state. Thus, although the VCCSD(SD) surface is lacking as compared to MRMP2, we see that it is reasonably similar to CCSD, even in this difficult case.

Once again, we have demonstrated that VCCSD(SD) is rather faithful to CCSD, even in a very sensitive system. Unfortunately, in this example both methods are lacking compared to higher level calculations. Intriguingly, we notice that in many senses, the pure valence space contribution of VCCSD gives a better description of the surface than either CASSCF(6,6) or VCCSD(SD). This behavior could arise from either of two key effects: the increased size of the active space relative to the CASSCF calculations, or the incomplete treatment of dynamical correlation in the truncated perturbative correction (SD). We hope to report on a more extensive analysis of these issues in the near future.

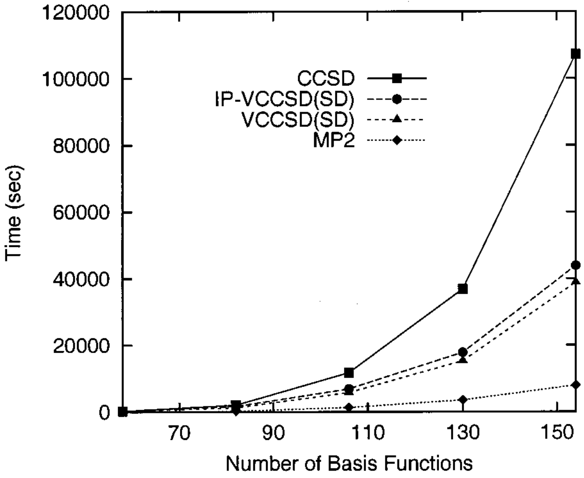

FIG. 5. Comparison of timings on growing linear alkane chains for various methods in the cc-pVDZ basis. In this figure, IP-VCCSD(SD) refers to the time of both the IP calculation and the VCCSD(SD) calculation, while VCCSD(SD) includes only the actual VCCSD(SD) steps.

F. Timings

As discussed in the Introduction, the purpose of this paper is to assess the capability of a valence-based method to approximate CCSD. Future work will more fully exploit the potential efficiency of this approach. For the moment, we content ourselves with a simple preliminary comparison of the efficiency of such a method against standard methods. VCCSD(SD) and CCSD calculations on a growing linear alkane chain in the cc-pVDZ basis were performed and the timings noted, as is plotted in Fig. 5. In all molecules in this set, the VCCSD(SD) calculation (including the time required to obtain the IP orbitals) is faster than the full CCSD calculation. The savings become more pronounced at larger system sizes, as expected. By comparing the timings of VCCSD(SD) with and without the IP calculation, one can see that obtaining the IP orbitals does not correspond to too large a fraction of the total computational time, which was one of the major goals of this study. Of course, the cost of an MP2 calculation is still far below that of the VCCSD(SD) calculation. The next step, which we hope to report on in the future, is to apply local correlation approximations to both the valence part of the problem and the second-order correction to generate a method well suited to treating larger systems.

IV. CONCLUSIONS

This study has explored the validity of partitioning the correlation energy into static and dynamical contributions to approximate a correlation method (CCSD) which makes no such distinction. Such an approximation has the potential to be significantly more efficient if it is sufficiently accurate. Our model uses CCSD in the perfect-pairing active space of all valence electrons, plus a truncated perturbative (2) correction for nonvalence single and double substitutions. If appropriately optimized orbitals are employed, this VCCSD(SD) model approximates full CCSD fairly satisfactorily for spectroscopic constants, structural properties, relative energies, and in the Cope rearrangement. Residual deviations are likely to be largely the result of neglected effects of coupling between the correlation effects in the valence and nonvalence space. Having demonstrated that such an approach can be successful, future work will be directed towards efficient local correlation treatments based on this framework.

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[1] M. Head-Gordon, J. Phys. Chem. **100**, 13213 (1996).
[2] S. Saebø and P. Pulay, Theor. Chim. Acta **69**, 357 (1986).
[3] S. Saebø and P. Pulay, Annu. Rev. Phys. Chem. **44**, 213 (1993), and references cited therein.
[4] M. Schütz, G. Hetzer, and H.-J. Werner, J. Chem. Phys. **111**, 5691 (1999).
[5] M. S. Lee, P. E. Maslen, and M. Head-Gordon, J. Chem. Phys. **112**, 3592 (2000).
[6] P. Y. Ayala and G. E. Scuseria, J. Chem. Phys. **110**, 3660 (1999).
[7] P. Pulay, S. Saebø, and K. Wolinski, Chem. Phys. Lett. **344**, 543 (2001).
[8] K. Andersson, P.-A. Malmqvist, B. O. Roos, A. Sadlej, and K. Wolinski, J. Phys. Chem. **94**, 5483 (1990).
[9] T. Helgaker, P. Jørgensen, and J. Olsen, *Molecular Electronic-Structure Theory* (Wiley, Chichester, England, 2000), p. 599.
[10] S. R. Gwaltney and M. Head-Gordon, Chem. Phys. Lett. **323**, 21 (2000).
[11] S. R. Gwaltney, C. D. Sherrill, M. Head-Gordon, and A. I. Krylov, J. Chem. Phys. **113**, 3548 (2000).
[12] S. R. Gwaltney and M. Head-Gordon, J. Chem. Phys. **115**, 2014 (2001).
[13] S. R. Gwaltney, E. F. C. Byrd, T. Van Voorhis, and M. Head-Gordon, Chem. Phys. Lett. **353**, 359 (2002).
[14] A. C. Hurley, J. Lennard-Jones, and J. A. Pople, Proc. R. Soc. London, Ser. A **220**, 446 (1953).
[15] W. J. Hunt, P. J. Hay, and W. A. Goddard III, J. Chem. Phys. **57**, 738 (1972).
[16] W. A. Goddard III and L. B. Harding, Annu. Rev. Phys. Chem. **29**, 363 (1978).
[17] F. B. Bobrowicz and W. A. Goddard, *Methods of Electronic Structure Theory* 3, edited by H. F. Schaefer III (Plenum, New York, 1977).
[18] T. Van Voorhis and M. Head-Gordon, Chem. Phys. Lett. **317**, 575 (2000).
[19] T. Van Voorhis and M. Head-Gordon, J. Chem. Phys. **112**, 5633 (2000).
[20] T. Van Voorhis and M. Head-Gordon, J. Chem. Phys. **115**, 7814 (2001).
[21] A. I. Krylov, C. D. Sherrill, E. F. C. Byrd, and M. Head-Gordon, J. Chem. Phys. **109**, 10669 (1998).
[22] T. Van Voorhis and M. Head-Gordon, Chem. Phys. Lett. **330**, 585 (2000).
[23] I. I. Ukrainskii, Theor. Math. Phys. **32**, 816 (1978).
[24] J. Cullen, Chem. Phys. **202**, 217 (1996).
[25] K. Raghavachari, G. Trucks, J. A. Pople, and M. Head-Gordon, Chem. Phys. Lett. **157**, 479 (1989).
[26] J. Kong, C. A. White, A. I. Krylov *et al.*, J. Comput. Chem. **21**, 1532 (2000).
[27] T. H. Dunning, Jr., J. Chem. Phys. **90**, 1007 (1989).
[28] Basis sets were obtained from the Extensible Computational Chemistry Environment Basis Set Database, Version 10/12/01, as developed and distributed by the Molecular Science Computing Facility, Environmental and Molecular Sciences Laboratory which is part of the Pacific Northwest Laboratory, P.O. Box 999, Richland, WA 99352, and funded by the U.S. Department of Energy. The pacific Northwest Laboratory is a multiprogram laboratory operated by Battelle Memorial Institute for the U.S. Department of Energy under Contract No. DE-AC06-76LO 1830. Contact David Feller or Karen Schuchardt for further information.
[29] K. P. Huber and G. Herzberg, *Molecular Spectra and Molecular Structure IV. Constants of Diatomic Molecules* (Van-Nostrand Reinhold, New York, 1979).
[30] T. D. Crawford, C. D. Sherrill, E. F. Valeev *et al.*, PSI 3.0, development version, PSITECH, Inc., Watkinsville, GA 30677, 2000.
[31] D. E. Woon and T. H. Dunning, Jr, J. Chem. Phys. **103**, 4572 (1995).
[32] T. H. Dunning, Jr., K. A. Peterson, and A. K. Wilson, J. Chem. Phys. **114**, 9244 (2001).
[33] R. Krishnan, J. Binkley, R. Seeger, and J. Pople, J. Chem. Phys. **72**, 650 (1980).
[34] A. McLean and G. Chandler, J. Chem. Phys. **72**, 5639 (1980).
[35] K. L. Bak, P. Jørgensen, J. Olsen, T. Helgaker, and W. Klopper, J. Chem. Phys. **112**, 9229 (2000).
[36] K. L. Bak, J. Gauss, P. Jørgensen, J. Olsen, T. Helgaker, and J. F. Stanton, J. Chem. Phys. **114**, 6548 (2001).
[37] M. J. S. Dewar and C. Jie, J. Am. Chem. Soc. **109**, 5893 (1987).
[38] M. Dupuis, C. Murray, and E. R. Davidson, J. Am. Chem. Soc. **113**, 9756 (1991).
[39] D. A. Hrovat, K. Morokuma, and W. T. Borden, J. Am. Chem. Soc. **116**, 1072 (1994).
[40] P. M. Kozlowski, M. Dupuis, and E. R. Davidson, J. Am. Chem. Soc. **117**, 774 (1995).
[41] W. T. Borden and E. R. Davidson, Acc. Chem. Res. **29**, 67 (1996).
[42] V. N. Staroverov and E. R. Davidson, J. Mol. Struct.: THEOCHEM **573**, 81 (2001).
[43] E. R. Davidson, J. Phys. Chem. **100**, 6161 (1996).
[44] W. J. Hehre, R. Ditchfield, and J. A. Pople, J. Chem. Phys. **56**, 2257 (1972).
[45] P. C. Hariharan and J. A. Pople, Theor. Chim. Acta **28**, 213 (1973).